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SOLID MINERAL FUELS

DETERMINATION OF GROSS CALORIFIC VALUE BY THE CALORIMETRIC BOMB METHOD, AND CALCULATION OF NET CALORIFIC VALUE

1st EDITION

April 1971

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BRIEF HISTORY

The ISO Recommendation R 1928, *Solid mineral fuels – Determination of gross calorific value by the calorimetric bomb method, and calculation of net calorific value*, was drawn up by Technical Committee ISO/TC 27, *Solid mineral fuels*, the Secretariat of which is held by the British Standards Institution (BSI).

Work on this question led to the adoption of Draft ISO Recommendation No. 1928, which was circulated to all the ISO Member Bodies for enquiry in December 1969. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Australia	Iran	Thailand
Belgium	Netherlands	Turkey
Canada	Portugal	U.A.R.
Chile	Romania	United Kingdom
Czechoslovakia	South Africa, Rep. of	U.S.A.
Denmark	Spain	U.S.S.R.
France	Sweden	Yugoslavia
Greece	Switzerland	

The following Member Bodies opposed the approval of the Draft :

Germany
Poland

This Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided to accept it as an ISO RECOMMENDATION.

CONTENTS

ISO Recommendation | R 1928 | April 1971

SOLID MINERAL FUELS

DETERMINATION OF GROSS CALORIFIC VALUE BY THE CALORIMETER BOMB METHOD, AND CALCULATION OF NET CALORIFIC VALUE

1. SCOPE

This ISO Recommendation describes the determination of the gross calorific value of a solid fuel at constant volume in an adiabatic, an isothermal, or a static bomb calorimeter.

The result obtained by this method is the gross calorific value of the analysis sample at constant volume, the water of the combustion products being condensed to liquid at the calorimeter temperature. In practice, fuel is burned at constant (atmospheric) pressure and the water is not condensed but is removed, as vapour, with the flue gases. Under these conditions the operative heat of combustion is the net calorific value of the fuel at constant pressure. The net calorific value at constant volume may also be used; formulae for calculating both values are given.

2. DEFINITIONS

2.1 *Unit of heat* : The absolute joule (J).

$$
\begin{aligned}
1\ \text{J} &= 1\ \text{newton metre (N·m)}\\
&= 1 \times 10^{7}\ \text{ergs}\\
&= 0.238\,846\ \text{International Table calories } (\text{cal}_{\text{IT}})\\
(1\ \text{cal}_{\text{IT}} &= 4.1868\ \text{J})
\end{aligned}
$$

2.2 *Unit of temperature* : The kelvin (K)

1 K = a temperature interval of 1 degree Celsius.

The international reference temperature for thermochemistry of 25 °C is used as the reference temperature for calorific value, though the temperature dependence of the calorific value of coal or coke is small [about 1 J/(g.K)].

2.3 *Gross calorific value at constant volume.* The number of heat units measured as being liberated when unit mass of solid fuel is burned in oxygen in a bomb under standard conditions; the materials after combustion are taken to consist of the gases oxygen, carbon dioxide, sulphur dioxide and nitrogen, liquid water in equilibrium with its vapour and saturated with carbon dioxide, and solid ash.

2.4 *Net calorific value at constant volume.* The number of heat units which would be liberated if unit mass of the fuel were burned in oxygen under conditions of constant volume, the residual materials being taken as oxygen, carbon dioxide, sulphur dioxide, nitrogen, water vapour and ash, all at 25 °C.

2.5 *Net calorific value at constant pressure.* The number of heat units which would be liberated if unit mass of the fuel were burned in oxygen under conditions of constant pressure, the residual materials being taken as oxygen, carbon dioxide, sulphur dioxide, nitrogen, water vapour and ash, all at 25 °C.

2.6 *Effective heat capacity of the system.* The heat required to cause unit rise of temperature in the calorimeter system under the conditions of a calorimetric determination.

3. PRINCIPLE

3.1 Gross calorific value

A weighed portion of the sample of solid fuel is burned in oxygen in a bomb calorimeter under standardized conditions. The gross calorific value is calculated from the temperature rise of the water in the calorimeter vessel and the mean effective heat capacity of the system. Allowances are made for the heat released by the ignition fuse, for thermochemical corrections and, where appropriate, for heat losses from the calorimeter to the water jacket.

3.2 Net calorific value

The net calorific value at constant volume and the net calorific value at constant pressure of a fuel are obtained by calculation from the gross calorific value at constant volume determined on the analysis sample. The calculation of the net calorific value at constant volume requires a knowledge of the moisture and hydrogen contents of the analysis sample; the calculation of the net calorific value at constant pressure requires, in addition, a knowledge of the oxygen content of the analysis sample.

4. REAGENTS

4.1 *Oxygen* at a pressure capable of filling the bomb to 30 bar and free from combustible matter (oxygen made by the electrolytic process may contain up to 4 % of hydrogen and is therefore unsuitable).

4.2 *Fuse* :

Firing wire :	nickel-chromium	0.16 to 0.20 mm diameter *or*
	platinum	0.06 to 0.10 mm diameter
Cotton :	white cellulose cotton.	

4.3 *Paste*. Fused aluminosilicate cement passing a 63 μm test sieve and suitable for use up to a temperature of 1400 °C, mixed with water.

4.4 *Alumina*. Fused alumina of analytical reagent quality, passing a 180 μm sieve and retained on a 106 μm sieve.

4.5 *Reagent solutions*

4.5.1 *Barium hydroxide* solution 0.1 N.

4.5.2 *Sodium carbonate* solution 0.1 N.

4.5.3 *Sodium hydroxide* solution 0.1 N.

4.5.4 *Hydrochloric acid* solution 0.1 N.

4.6 *Coloured indicators*

4.6.1 *Screened methyl orange indicator* solution, 1 g/l.

Dissolve 0.25 g of methyl orange and 0.15 g of xylene cyanol FF in 50 ml of 95 % (V/V) ethanol and dilute to 250 ml with water.

4.6.2 *Phenolphthalein* solution, 10 g/l.

Dissolve 2.5 g of phenolphthalein in 250 ml of 95 % (V/V) ethanol.

4.7 *Thermochemical standard.* Dry benzoic acid of thermochemical standard certified by a national testing authority.

After pelleting the benzoic acid, the pellets should be dried before use by exposing them for at least 3 days in a desiccator containing magnesium perchlorate. Alternatively, transfer about 1.2 g of the benzoic acid into a crucible, previously weighed to 0.1 mg, and heat at 121 to 126 °C for 1 hour; after cooling in a desiccator, reweigh the crucible and contents to 0.1 mg to obtain the mass of dry benzoic acid taken.

The heat of combustion of the benzoic acid listed in the certificate for the conditions of use should be adopted in calculating the effective heat capacity of a calorimeter.

5. APPARATUS

5.1 *Bomb*, capable of withstanding safely the pressures developed during combustion. The design should permit complete recovery of all liquid products. The materials of construction should resist corrosion by the acids produced by the combustion of coal or coke.

NOTE. – Bomb parts should be inspected regularly for wear and corrosion; particular attention should be paid to the condition of the threads of the main closure.

5.2 *Calorimeter*, made of metal, highly polished on the outside and capable of holding sufficient water to cover completely the flat upper surface of the bomb while the water is being stirred.

5.3 *Stirrer*, driven at a constant speed. The stirrer shaft should contain a non-conducting section below the cover of the water jacket to minimize the transmission of heat to or from the system. If a cover is used for the calorimeter vessel, the non-conducting section should be above this cover.

NOTE. – For isothermal and static bomb calorimeters the rate of stirring should ensure that the length of the chief period (see clause 7.2) in determinations of effective heat capacity using benzoic acid (see Annex) does not exceed 10 minutes.

5.4 *Water jacket*, which may be an adiabatic, isothermal or static type, enclosing the calorimeter vessel with an air-gap of approximately 10 mm separating the vessel and water jacket.

The adiabatic water jacket should have either electrode or immersion heaters capable of supplying energy at a rate sufficient to maintain the temperature of the water in the jacket within 0.1 K of that of the calorimeter vessel after the charge has been fired. When in balance at 25 °C, the temperature drift of the calorimeter vessel should not exceed 0.0005 K/min.

The isothermal water jacket should be provided with a means of keeping its temperature constant to ± 0.1 K.

The static water jacket should have a thermal capacity big enough to restrict changes of temperature of the water in it. From the time of firing the charge to the end of the after-period or during a period of 15 minutes, whichever is the greater, with a cooling constant (d) of 0.0020 (see clause 8.2), the rise in temperature of the water in the jacket should be less than 0.16 K; with a cooling constant (d) of 0.0030, the rise in temperature should be less than 0.11 K.

NOTE. – For an insulated metal jacket this can be ensured by making the capacity at least 12.5 litres, contained in a wide annular jacket.

5.5 *Temperature measuring instrument*, capable of indicating temperatures which when corrected have an accuracy of 0.002 K, so that temperature intervals of 2 to 3 K can be determined with an accuracy of 0.004 K. It should be calibrated against a known standard by a national testing authority, at intervals not larger than 0.5 K over the range of use or, for mercury-in-glass thermometers, over the whole graduated scale.

(1) Resistance thermometers composed of a platinum resistance, resistance bridge and galvanometer may be used.

(2) Mercury-in-glass thermometers which conform to the following ISO Recommendations are suitable :

ISO/R 651, *Solid stem calorimeter thermometers*;

ISO/R 652, *Enclosed-scale calorimeter thermometers*;

ISO/R . . .*, *Solid stem adjustable range thermometers*;

ISO/R . . .*, *Enclosed-scale adjustable range thermometers*.

A viewer with about X 5 magnification is needed for reading the temperature to the required accuracy.

A mechanical vibrator to tap the thermometer for a period of about 10 seconds before reading the temperature is desirable to prevent sticking of the mercury column; if this is not available, the thermometer should be tapped manually, for example with a pencil.

* At present at the stage of draft proposal.

5.6 *Crucible*, of silica, nickel-chromium or platinum.

For coal, it should be about 25 mm in diameter, flat based and not more than 20 mm deep. Silica crucibles should be about 1.5 mm thick and metal crucibles about 0.5 mm thick. A shallow crucible of nickel-chromium foil about 0.25 mm thick is recommended when testing high ash coals, in order to reduce any error from incomplete combustion.

For coke, the nickel-chromium crucible, as described for use with coal, should be lined with a paste of fused aluminosilicate cement (see clause 4.3). After drying at 50 to 60 °C, the excess cement is scraped off to leave a smooth lining about 1.5 mm thick; the crucible is then incinerated at 1000 °C for 2 hours. Before use, 0.3 g of alumina (see clause 4.4) is spread over the base of the lined crucible and compacted with the flat end of a metal rod.

For benzoic acid, either of the crucibles specified for coal is suitable. If smears of unburned carbon occur, a smaller nickel-chromium crucible, for example 0.25 mm thick, 15 mm in diameter and 7 mm deep, may be used.

5.7 *Ignition circuit*. The electrical supply should be 6 to 12 V alternating current from a step-down transformer or direct current from batteries. It is desirable to include an ammeter or pilot light in the circuit to indicate when current is flowing.

The firing switch should be of the spring-loaded, normally open type.

CAUTION. – The firing switch should not be mounted on the calorimeter.

5.8 *Ancillary pressure equipment*

5.8.1 *Pressure regulator* to control the filling of the bomb with oxygen.

5.8.2 *Pressure gauge* (0 to 50 bar) to indicate the pressure in the bomb.

5.8.3 *Relief valve* or *bursting disk* operating at 35 bar installed in the filling line, to prevent overfilling the bomb.

WARNING. – Equipment for high pressure oxygen must be kept free from oil and grease. Do not test or calibrate the pressure gauge with hydrocarbon fluid.

5.9 *Timer*, fitted in a convenient place, indicating minutes and seconds. It may usefully incorporate a device giving audible signals lasting 10 seconds starting at 1 minute intervals.

6. SAMPLE

The coal or coke used for the determination of calorific value should be the analysis sample ground to pass a sieve of 200 μm aperture. The sample should be exposed in a thin layer for the minimum time necessary for the moisture content to reach approximate equilibrium with the laboratory atmosphere.

The sample should be mixed, preferably by mechanical means, immediately before the determination. Portions for duplicate determinations should be weighed out at the same time. The moisture content of the sample should be determined at the same time as the determination of calorific value, so that the appropriate correction can be made.

7. PROCEDURE

7.1 Adiabatic calorimeter

Weigh the crucible (see clause 5.6) to the nearest 0.1 mg and introduce into it sufficient of the sample to cause a temperature rise of 2 to 3 K (see Note 1, page 10). Weigh the crucible and contents to determine the mass of sample taken.

Connect a piece of firing wire tautly across the terminals of the bomb. Tie a known mass of cotton to the firing wire (see Note 2, page 10); arrange the ends of the cotton so that they touch the sample.

Put 5 ml of distilled water in the bomb. Assemble the bomb and charge it slowly with oxygen to a pressure of 30 bar without displacing the original air. If the bomb is inadvertently charged with oxygen above 33 bar, discard the test and begin again.

Put sufficient water in the calorimeter vessel to cover the flat upper surface of the bomb cap. This quantity of water should be the same, to within 1 g, as that used in determining the mean effective heat capacity of the calorimeter (see Annex). Transfer the calorimeter vessel to the water jacket; lower the bomb into the calorimeter vessel and check that the bomb is gas-tight. If gas escapes from the bomb, discard the test, eliminate the cause of leakage and begin again.

Assemble and start up the apparatus. Use a constant rate of stirring such that the length of the predetermined interval (see Annex, section A.4) does not exceed 10 minutes. Select the setting of the bridge circuit that will result in the minimum drift in the temperature of the calorimeter vessel at the final temperature:

After 10 minutes tap the thermometer lightly and read it to 0.001 K (the "firing temperature", t_o). Fire the charge; hold the switch closed only long enough to ignite the fuse.

CAUTION. – Do not extend any part of the body over the calorimeter during firing, nor for 20 seconds thereafter.

After the predetermined interval, established when the effective heat capacity of the system is determined (see Annex), tap the thermometer again and read it to 0.001 K (the "final temperature", t_n). The observer should take care to avoid parallax errors when using the magnifying viewer to read mercury-in-glass thermometers.

Remove the bomb from the calorimeter vessel, release the pressure and dismantle the bomb. Examine the bomb interior and discard the test if unburned sample or a sooty deposit is visible.

When certain unreactive cokes are tested, the residue in the bomb frequently contains detectable unburned sample. A correction to be applied for such persistently incomplete combustion may be calculated from the amount of unburned carbon, which may be estimated by the procedure described in Note 3, page 10.

Wash the contents of the bomb into a beaker with distilled water. Wash the underside of the bomb cap and the outside of the crucible with distilled water; add the washings to the beaker. Dilute to approximately 100 ml and boil to expel carbon dioxide. While still hot, titrate with the barium hydroxide solution (4.5.1) using the phenolphthalein solution (4.6.2) as indicator. Add 20 ml of the sodium carbonate solution (4.5.2), filter the warm solution and wash the precipitate with distilled water. When cold, titrate the filtrate with the hydrochloric acid solution (4.5.4), using the screened methyl orange solution (4.6.1) as indicator, ignoring the phenolphthalein colour change. (These titrations may be omitted if the sulphur content of the coal and the nitric acid correction are known – see Note 4, page 11).

7.2 Isothermal and static calorimeters

Weigh the crucible (see clause 5.6) to the nearest 0.1 mg and introduce into it sufficient of the sample to cause a temperature rise of 2 to 3 K (see Note 1, page 10). Weigh the crucible and contents to determine the mass of sample taken.

Connect a piece of firing wire tautly across the terminals of the bomb. Tie a known mass of cotton to the firing wire (see Note 2, page 10); arrange the ends of the cotton so that they touch the sample.

Put 5 ml of distilled water in the bomb. Assemble the bomb and charge it slowly with oxygen to a pressure of 30 bar without displacing the original air. If the bomb is inadvertently charged with oxygen above 33 bar, discard the test and begin again.

Put sufficient water in the calorimeter vessel to cover the flat upper surface of the bomb cap. This quantity of water should be the same, to within 1 g, as that used in determining the mean effective heat capacity. The initial temperature of the water should be such that, at the end of the chief period, the temperature will not exceed that of the water in the jacket by more than 0.5 K. Transfer the calorimeter vessel to the water jacket; lower the bomb into the calorimeter vessel and check that the bomb is gas-tight. If gas escapes from the bomb, discard the test, eliminate the cause of leakage and begin again.

Assemble the apparatus. Start the stirrer and keep in operation at a constant rate throughout the determination. Stir for at least 10 minutes before starting to read the temperature (see Note 5, page 11). Read the temperature to 0.001 K and continue to do so at intervals of 1 minute for a period of 5 minutes. Tap the thermometer lightly for 10 seconds before each reading; take care to avoid parallax errors when using the magnifying viewer to read mercury-in-glass thermometers. Fire the charge immediately after reading the last temperature in the preliminary period (see (1) below); hold the switch closed only long enough to ignite the fuse.

CAUTION. – Do not extend any part of the body over the calorimeter during firing,nor for 20 seconds thereafter.

(1) *Preliminary period.* If the average deviation of the values of the rate of change of temperature during this period of 5 minutes exceeds 0.001 K/min (see Note 6, page 11), continue to read the thermometer at 1 minute intervals until the average deviation is less than 0.001 K/min for a period of 5 minutes.

The last temperature of the *preliminary period* is the initial temperature of the *chief period* (t_o).

(2) *Chief period.* During the first few minutes of the chief period it will not be possible to read the thermometer to 0.001 K but readings to this precision should be resumed as soon as possible and continued to the end of the test. The chief period does not necessarily end with the attainment of maximum temperature; the end is assessed as the point at which the *after-period* begins.

(3) *After-period.* The after-period begins at the point when, for a subsequent 5 minute period, the average deviation of the individual values of change of temperature per minute is not more than 0.001 K (see Note 6, page 11).

Remove the bomb from the calorimeter vessel, release the pressure and dismantle the bomb. Examine the bomb interior and discard the test if unburned sample or a sooty deposit is visible.

When certain unreactive cokes are tested, the residue in the bomb frequently contains detectable unburned sample. A correction to be applied for such persistently incomplete combustion may be calculated from the amount of unburned carbon, which may be estimated by the procedure described in Note 3, below.

Wash the contents of the bomb into a beaker with distilled water. Wash the underside of the bomb cap and the outside of the crucible with distilled water; add the washings to the beaker. Dilute to approximately 100 ml and boil to expel carbon dioxide. While still hot, titrate with the barium hydroxide solution (4.5.1) using the phenolphthalein solution (4.6.2) as indicator. Add 20 ml of the sodium carbonate solution (4.5.2), filter the warm solution and wash the precipitate with distilled water. When cold, titrate the filtrate with the hydrochloric acid solution (4.5.4), using the screened methyl orange solution (4.6.1) as indicator, ignoring the phenolphthalein colour change. (These titrations may be omitted if the sulphur content of the coal and the nitric acid correction are known – see Note 4, page 11.)

NOTES

1. Normally 1 g of coal will be taken. For high ash coals, the use of 0.75 g of the sample and the shallow crucible of nickel-chromium foil (see clause 5.6) should reduce the possibility of incomplete combustion.
2. For convenience, a measured length of cotton of known mass per unit length may be used; the length used in each determination of calorific value should be the same as was used in the determination of the effective heat capacity of the system.
3. The unburned carbon in the crucible may be estimated as follows : transfer the contents of the crucible (not the lining) to a silica or porcelain dish and dry for 1 hour at 320 °C. Cool, weigh the dish and its contents to the nearest 0.1 mg, heat at 815 °C for 1 hour, cool and reweigh to determine the loss in mass. The loss is taken to be unburned carbon. Alternatively the unburned carbon may be determined by one of the methods described in ISO Recommendations R 609 or R 625*. Should more than 6 mg of unburned carbon be found, the correction will be invalid and the determination of calorific value should be repeated.

* ISO/R 609, *Determination of carbon and hydrogen in coal and coke by the high temperature combustion method.*

ISO/R 625, *Determination of carbon and hydrogen in coal and coke by the Liebig method.*

4. For any given bomb, under constant conditions of heat release, the quantity of nitric acid formed, and therefore the consequent correction, is relatively constant; for hard coals in general, a typical value would be 33 J and for anthracite 25 J. After the value has been firmly established it may be applied in subsequent tests as an alternative to its determination. The determination of the sulphuric acid correction may then be shortened as follows :

   Titrate the warm (not boiling) bomb washings with the 0.1 N sodium hydroxide solution (4.5.3), using the screened methyl orange solution (4.6.1) as indicator, to determine the total acidity. Deduct from this titre (in millilitres) 0.7 times the nitric acid correction in joules, to obtain the volume of 0.1 N sulphuric acid present.

   If the sulphur content of the sample and the appropriate nitric acid correction are both known, the titration of the acids in the bomb washings is unnecessary. The sulphuric acid correction is equal to 9.5 J per milligramme of sulphur in the mass of coal used for determination of calorific value.

5. If the Regnault-Pfaundler cooling correction (see clause 8.2) is to be calculated the procedure described should be adopted; if an alternative formula, which is equivalent and acceptable, is to be used, some of the temperature readings may not be required and the procedure should be modified accordingly.

6. A convenient method of checking that the average deviation of the rate of change of temperature during the preliminary period and the after-period is within the specified limit is to list the five differences as units without the decimal place, code them by subtracting the smallest and arrange the coded differences in descending sequence. If the sequence is listed in the following Table, the average deviation is within the specified limit.

Table of acceptable difference sequences

Coded difference	Average deviation $\times 10^3$	Coded difference	Average deviation $\times 10^3$	Coded difference	Average deviation $\times 10^3$
10000	0.32	22000	0.96	31100	0.80
11000	0.48	22100	0.80	31110	0.72
11100	0.48	22110	0.64	32110	0.88
11110	0.32	22200	0.96	32210	0.88
20000	0.64	22210	0.72	32220	0.72
21000	0.72	22220	0.64	33220	0.80
21100	0.64	30000	0.96	33320	0.96
21110	0.40	31000	0.96	33330	0.96

Example :

Time minutes	Temperature °C	Difference (units)	Coded difference
0	24.157		
		7	2
1	24.164		
		5	0
2	24.169		
		8	3
3	24.177		
		8	3
4	24.185		
		7	2
5	24.192		

The sequence 33220 is acceptable.

8. CORRECTIONS

The following corrections are made to the experimental observations :

8.1 Thermometer corrections

If a mercury-in-glass thermometer is used the corrections prescribed in the certificate issued with the thermometer are applied to the observed firing temperature, t_o, and the final temperature, t_n.

8.2 Cooling correction

The heat loss to the water jacket is negligible in an adiabatic calorimeter such as is specified and a cooling correction is not necessary.

The heat lost to the water jacket of an isothermal or static calorimeter may be compensated by an addition to the temperature rise. This correcting addition may be calculated by the Regnault-Pfaundler formula or by any formula which is equivalent to it and which is accepted as such by a national standardizing body.

Regnault-Pfaundler formula

Cooling correction

$$= nv' + \frac{v'' - v'}{t'' - t'} \left[\sum_{1}^{n-1}(t) + \tfrac{1}{2}(t_o + t_n) - nt' \right]$$

$$= nv' + dS$$

where

n is the number of minutes in the chief period;

v' is the rate of fall of temperature per minute in the preliminary period (if the temperature is rising, v' is negative, i.e. it should be added);

v'' is the rate of fall of temperature per minute in the after-period;

t' is the average temperature during the preliminary period;

t'' is the average temperature during the after-period;

t_o is the firing temperature;

$t_1, t_2, t_3 \ldots t_n$ are the successive temperatures recorded during the chief period, t_n being the first temperature after which the rate of change is constant within the defined limits;

$\sum_{1}^{n-1}(t)$ is the sum of $t_1, t_2, t_3 \ldots t_{n-1}$;

$d = \frac{v'' - v'}{t'' - t'}$, the "cooling constant" in min^{-1} of the calorimeter, which must be determined for each set of conditions;

$S =$ the expression in brackets.

8.3 Heat of ignition

The heat release from the cotton and firing wire is subtracted from the total heat released. The heat release from the cotton is calculated from its mass (dried at 100 °C) and the calorific value of cellulose (17 500 J/g). The heat release from the firing wire is calculated from the mass of a piece of wire equal in length to the distance between the poles of the bomb, allowing 1 400 J/g for nickel-chromium wire or 420 J/g for platinum wire.

8.4 Correction for heat of formation of acids

The heat gain due to the formation of sulphuric acid and nitric acid is subtracted from the total heat released. These corrections amount to 15.1 J/ml of 0.1 N sulphuric acid and 6.0 J/ml of 0.1 N nitric acid present in the bomb washings (see Note 4, page 11).

If a is the volume, in millilitres, of 0.1 N hydrochloric acid used, and

b is the volume, in millilitres, of 0.1 N barium hydroxide solution used,

then the sulphuric acid correction, in joules,

$$= 15.1(a + b - 20)$$

and the nitric acid correction, in joules,

$$= 6.0\,(20 - a)$$

The sum of these two may be calculated directly from the formula :

$$\text{total correction (joules)} = 9.1\,a + 15.1\,b - 181.7$$

8.5 Correction for unburned carbon (coke only)

The loss in mass on ignition of the residue from the coke crucible is taken to be unburned carbon. Its heat equivalent, on the basis of 1 mg ≙ 33.5 J, is added to the determined heat release.

9. CALCULATION AND EXPRESSION OF RESULTS

9.1 Calculation

Compute the gross calorific value at constant volume from the observations by substituting into the equation :

$$Q_{gr,v} = \frac{(\Delta\theta)\,\overline{C}_{(5)} - e_1 - e_2 - e_3 - e_4}{m_f}$$

where

$Q_{gr,v}$ is the gross calorific value at constant volume of the coal as analysed, in joules per gramme;

$\Delta\theta$ is the corrected temperature rise.
This is calculated from the observed firing temperature (t_o), corrected for thermometer error, and the observed final temperature (t_n), corrected for thermometer error, plus the cooling correction calculated for isothermal and static calorimeters;

$\overline{C}_{(5)}$ is the mean of five determinations of effective heat capacity of the calorimeter, in joules per kelvin (see Annex);

e_1 is the correction for heat of combustion of the cotton, in joules;

e_2 is the correction for heat of combustion of the firing wire, in joules;

e_3 is the correction for heat of formation of sulphuric acid, in joules;

e_4 is the correction for heat of formation of nitric acid, in joules;

m_f is the mass of the sample of fuel, in grammes.

Examples to illustrate the method of calculating the results of a calorific determination are given in Appendix Y.

9.2 Reporting

The result (preferably the mean of duplicate determinations – see section 10) should be reported to the nearest 20 J/g.

10. PRECISION OF THE METHOD

Calorific value, gross, at constant volume	Maximum acceptable differences between results obtained on the analysis samples (calculated to the same moisture content)	
	in the same laboratory (Repeatability)	in different laboratories (Reproducibility)
	120 J/g	300 J/g

NOTE. – A moisture determination should be carried out simultaneously by one of the methods described in ISO Recommendations R 331, R 348 or R 687*.

10.1 Repeatability

The results of duplicate determinations carried out in the same laboratory by the same operator with the same apparatus on the same analysis sample should not differ by more than the above value.

10.2 Reproducibility

The means of the results of duplicate determinations carried out in each of two laboratories, on representative portions taken from the same sample at the last stage of sample preparation, should not differ by more than the above value.

10.3 Calculation to other bases

The calculation of results to other bases is the subject of ISO Recommendation R 1170**.

11. CALCULATION OF NET CALORIFIC VALUE

11.1 General

The result of the preceding determination is the gross calorific value of the fuel at constant volume. From this, the net calorific value at constant volume and the net calorific value at constant pressure may be calculated by the formulae given below.

The formulae take account of any change in the moisture basis that may be required. Calculation to other bases is described in ISO Recommendation R 1170**.

The derivations of the formulae are given in Appendix Z; the constants have been rounded off to yield a suitable precision.

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* ISO/R 331, *Determination of moisture in the analysis sample of coal by the direct gravimetric method.*
ISO/R 348, *Determination of moisture in the analysis sample of coal by the direct volumetric method.*
ISO/R 687, *Determination of moisture in the analysis sample of coke.*

** ISO/R 1170, *Calculation of coal and coke analyses to different bases.*

11.2 Net calorific value at constant volume

$$Q_{\mathrm{net,v,m}} = \left(Q_{\mathrm{gr,v}} - 206\,[H]\right) \times \frac{100 - M}{100 - M_1} - 23\,M$$

where

$Q_{\mathrm{net,v,m}}$ is the net calorific value at constant volume of the fuel with moisture content M, in joules per gramme;

$Q_{\mathrm{gr,v}}$ is the gross calorific value at constant volume of the analysis sample of the fuel, in joules per gramme;

$[H]$ is the percentage of hydrogen in the analysis sample (this includes the hydrogen present in the water of hydration of the mineral matter as well as that in the coal substance);

M is the percentage moisture content for which the calculation is required. On the dry basis, $M = 0$; on the air-dried basis, $M = M_1$; on the as-fired basis, M is the percentage of total moisture;

M_1 is the percentage of moisture in the analysis sample.

11.3 Net calorific value at constant pressure

$$Q_{\mathrm{net,p,m}} = \left(Q_{\mathrm{gr,v}} - 212\,[H] - 0.8\,[O]\right) \times \frac{100 - M}{100 - M_1} - 24.5\,M$$

where

$Q_{\mathrm{net,p,m}}$ is the net calorific value at constant pressure of the fuel with moisture content M, in joules per gramme;

$[O]$ is the percentage of oxygen in the analysis sample. It may be derived by subtracting from 100 the sum of the percentages of moisture, ash, carbon, hydrogen, nitrogen and sulphur.

NOTE. – A value for nitrogen typical of the fuel may be used; any error will be negligible.

ANNEX

DETERMINATION OF EFFECTIVE HEAT CAPACITY OF THE CALORIMETER

A.1 PRINCIPLE

A known mass of benzoic acid of certified calorific value is burned in oxygen in the bomb calorimeter. To the heat of combustion of the benzoic acid are added the heats of combustion of the cotton and the firing wire and the heat of formation of nitric acid.

At least five complete determinations of effective heat capacity are carried out. Provided that their range does not exceed 55 J/K, the mean of these five, $\overline{C}_{(5)}$, is taken for calculation of the calorific value of the fuel (see clause 9.1).

A.2 PROCEDURE

Proceed as described in section 7 for the determination of calorific value. If necessary use the small metal crucible specified in clause 5.6.

When determining the effective heat capacity of an adiabatic calorimeter, read the temperature at 1 minute intervals over a period of 10 minutes, commencing 5 minutes after firing the charge (see section A.4).

Dilute the bomb washings to approximately 50 ml with distilled water. Titrate the nitric acid directly with the sodium hydroxide solution (4.5.3) or the sodium carbonate solution (4.5.2), using the screened methyl orange solution (4.6.1) as indicator.

A.3 CALCULATION OF A SINGLE COMPLETE DETERMINATION

The effective heat capacity of the system is calculated from the formula :

$$C = \frac{m_b \left(Q^{b}_{gr,v}\right) + e_1 + e_2 + e_4}{\Delta\theta}$$

where

C is the effective heat capacity, in joules per kelvin;

m_b is the mass of the benzoic acid, in grammes;

$Q^{b}_{gr,v}$ is the certified gross calorific value of the benzoic acid at constant volume, in joules per gramme (see clause 4.6);

and $\Delta\theta$, e_1, e_2 and e_4 are as defined in clause 9.1.

NOTE. – e_4 = 6.0 times the volume, in millilitres, of the sodium hydroxide solution or the sodium carbonate solution used in titrating the bomb washings.

A.4 PREDETERMINED INTERVAL (Adiabatic calorimeters)

The period between the firing of the charge and the reading of the final temperature is the predetermined interval. It is calculated from the temperature readings taken at intervals of 1 minute in each determination of effective heat capacity.

From the recorded observations of each determination, note the shortest time in minutes from the firing of the charge to reaching the second of three consecutive readings which do not differ by more than 0.001 K. Calculate, to the nearest whole minute, the mean of the five values to obtain the length of the predetermined interval; this should not exceed 10 minutes.

Use the predetermined interval for all determinations of calorific value until a new value is established. It should be re-established when commissioning a new calorimeter and checked after changing any component.

A.5 RE-DETERMINATION OF THE MEAN EFFECTIVE HEAT CAPACITY

When any part of the system is changed, the mean effective heat capacity should be re-determined. It should also be re-determined at intervals of not longer than 6 months.

Where a change to the system is not involved, the re-determined mean should be within 20 J/K of that previously determined. If the difference is greater than 20 J/K, experimental procedures should be examined and carefully checked.

APPENDIX Y

EXAMPLES TO ILLUSTRATE A METHOD OF CALCULATING RESULTS

Y.1 ADIABATIC CALORIMETER

Mass of coal			= 0.9992 g
Volume of 0.1 N hydrochloric acid		(*a*)	= 13.0 ml
Volume of 0.1 N barium hydroxide solution		(*b*)	= 10.9 ml
Final temperature observed (t_n)	= 25.416 °C		
thermometer correction	= +0.011 K		
Firing temperature observed (t_o)	= 22.793 °C		
thermometer correction	= +0.017 K		
Temperature rise ($t_n - t_o$) corrected for thermometer inaccuracies			= 2.617 K
Mean effective heat capacity			= 10 370 K
Heat liberated (2.617 × 10 370)			= 27 138 J

Subtract :

Sulphuric acid correction = 15.1 (13.0 + 10.9 − 20)	= 59
Nitric acid correction = 6.0 (20 − 13.0)	= 42
Correction for cotton and firing wire	= 84
Correction for unburned carbon	= Nil

= 185 J

Heat from 0.9992 g of coal	= 26 953 J
Gross calorific value at constant volume	= 26 975 J/g
	= **26.98 GJ/t**

Y.2 ISOTHERMAL CALORIMETER

Temperature of water jacket = 25 °C
Mean effective heat capacity = 10 370 J/K

Mass of coal		= 0.9992 g
Volume of 0.1 N hydrochloric acid	(*a*)	= 13.0 ml
Volume of 0.1 N barium hydroxide solution	(*b*)	= 10.9 ml

Observed temperature readings :

Time	Temperature	Time	Temperature	Time	Temperature
minutes	°C	minutes	°C	minutes	°C
0	22.771	6	23.99	13	25.407 (t_n)
1	22.775	7	25.00	14	25.405
2	22.780	8	25.295	15	25.403
3	22.785	9	25.373	16	25.400
4	22.789	10	25.400	17	25.398
5	22.793 (t_o)	11	25.407	18	25.396
		12	25.408		

Cooling correction (Regnault-Pfaundler formula) :

$v' = -0.0044$ $n = 8$ $v'' = 0.0022$

$t' = 22.782$ $t'' = 25.402$

$d = \frac{0.0066}{2.620}$ $\sum_{1}^{n-1}(t) = 175.873$

$= 0.00252$

$\frac{1}{2}(t_o + t_n) = 24.100$

$-nt' = -182.256$

therefore $S = 17.717$

$dS = 0.0446$

$nv' = -0.0352$

Cooling correction $= dS + nv'$ $= 0.009$ K

Final temperature observed (t_n) = 25.407

thermometer correction = +0.011

Firing temperature observed (t_o) = 22.793

thermometer correction = +0.017

Temperature rise $(t_n - t_o)$ corrected for thermometer inaccuracies = 2.608 K

Cooling correction = +0.009 K

Corrected temperature rise = 2.617 K

Heat liberated (2.617 × 10 370) = 27 138 J

Subtract :

Sulphuric acid correction = 15.1 (13.0 + 10.9 − 20) = 59

Nitric acid correction = 6.0 (20 − 13.0) = 42

Correction for cotton and firing wire = 84

Correction for unburned carbon = Nil

= 185 J

Heat from 0.9992 g of coal = 26 953 J

Gross calorific value at constant volume = 26 975 J/g

= 26.98 GJ/t